Appendix D
Adjuvants
Boise-Sawtooth Invasive Plant Species Treatment EIS

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Adjuvants are specially designed chemicals that are added to an herbicide solution to modify the performance of the total spray mixture. Adjuvants are not regulated by the EPA in the same way that pesticides are. The EPA does not register or approve the labeling of spray adjuvants. Field testing is generally completed by the adjuvant manufacturer (Bakke 2007). Labels accompanying adjuvants describe their properties and prescribe use rates. Information on types of adjuvants to use can also be found on herbicide labels and in publications by university extension services (Prather et al. 2011, Zollinger 2012).

Adjuvants perform various functions, including: enhanced plant uptake of the herbicide; better mixing of otherwise incompatible herbicides; increased adhesion of the spray to plant surfaces; and reduced spray drift. In many herbicide products, adjuvants are included as part of the pre-mixed formulation as purchased. Applicators can also add adjuvants to spray mixtures prior to application.

For many pesticide products containing adjuvants as part of the formulation, the compounds are not explicitly identified on the label or the Material Safety Data Sheet (MSDS). Unless they are on one of US EPA's lists of more toxic chemicals, they do not have to be identified. The identity of these ingredients in a pesticide or adjuvant product is legally protected from full disclosure as "Confidential Business Information."

At least one adjuvant is known to pose hazards to aquatic wildlife—the surfactant used in the original formulation of RoundUp®, polyoxyethyleneamine (POEA). This surfactant is more toxic to aquatic life than the active ingredient glyphosate. The POEA adjuvant (Roundup Pro) will only be used in uplands where there is no potential for movement into aquatic systems. Within or near aquatic systems, only products labelled for aquatic application would be used. Adjuvants used on the Boise & Sawtooth National Forests are identified below in Table 1.

Adjuvants with low toxicity to wildlife include modified seed oils, alkyl ethoxylates, and silicones. The most commonly used adjuvant is marker dye and it is analyzed in "Use and Assessment of Marker Dyes Used With Herbicides" (Pepling, Howard, Durkin, 1997)

"Activator" adjuvants enhance activity of an herbicide's active ingredient, while **"special purpose or utility modifier"** adjuvants offset common problems occurring during application, including poor water quality or foam produced during agitation of the spray mixture (Bakke 2007). Many adjuvants have properties that place them on a continuum between these two definitions and function both as activators and utility modifiers. Special purpose or utility adjuvants are used to offset or correct certain conditions associated with mixing and application such as impurities in the spray solution, extreme pH levels, and drift. These adjuvants include acidifiers, buffering agents, water conditioners, anti-foaming agents, compatibility agents, and drift control agents. Acidifiers enhance absorption of weak acid type herbicides. Drift reduction agents will generally increase the average droplet size. Defoamers reduce foaming that occurs during agitation of the spray mixture. Colorants or dyes help applicators determine what area was treated. This helps to prevent skips and overlaps and treatment of non-target areas. They reduce the chance of human exposure to recently treated vegetation (Bakke 2007).

Surfactants (surface active agents) are a broad category of activator adjuvants designed to improve or facilitate the dispersing/emulsifying, absorbing, spreading, sticking and/or pest-penetrating properties of the spray mixture. Pure water will stand as a droplet, with a small area of contact with the waxy leaf surface. Water droplets containing a surfactant will spread in a thin layer over a waxy leaf surface (Bakke 2007).

Post-emergence herbicide effectiveness depends on spray droplet retention and herbicide absorption by weed foliage. Adjuvants and spray water quality influence post-emergent herbicide

efficacy (USDA Custer National Forest 2006). Because post-emergence herbicide effectiveness is greatly influenced by plant factors such as age, size and the growing conditions encountered before application, herbicide performance can vary. A way to minimize the variations in post-emergence herbicide performance is to use an adjuvant or surfactant in the spray solution. Surfactants generally improve the effectiveness of post-emergence herbicides. Typically, surfactants are not added to herbicides that are soil applied (pre-emergence) (Zollinger 2012). Surfactants used on both Forests include non-ionic surfactants, methylated or ethylated vegetable oils, nitrogen sources, and organosilicone/silicone surfactants.

Non-ionic surfactants (NIS) are all-purpose surfactants comprised of linear or nonyl-phenol alcohols and/or fatty acids. This class of surfactant reduces surface tension of water and improves spreading, sticking and herbicide uptake (USDA Custer NF 2006). Often, non-ionic surfactants will have additional additive properties, as described on their label.

Methylated or Ethylated vegetable (seed) oils (MSO) are produced by reacting fatty acids from seed oils (corn, soybean, sunflower, and canola) with an alcohol to form esters. The methyl or ethyl esters produced by this reaction are combined with surfactants/emulsifiers to form esterified seed oil. These surfactants reduce surface tension of water and improve herbicide uptake by improving herbicide distribution on the leaf surface (USDA Custer NF 2006). Adverse environmental conditions such as low humidity, hot weather, lack of rain, drought-stressed weeds, or weeds not actively growing due to some environmental stress favor the use of MSO. These oils are more effective than non-ionic surfactants as an adjuvant to post-emergence herbicides (Zollinger 2012).

Nitrogen sources typically consist of premixed combinations of various forms of nitrogen and surfactants. They generally are used with herbicides recommending the addition of ammonium sulfate or 28 percent nitrogen. These surfactants reduce surface tension of water and improve leaf surface spreading (Miller and Westra 1998). They are used primarily with broadleaf herbicides. Fertilizers containing ammonium nitrogen have increased the effectiveness of herbicides like glyphosate, and 2, 4-D amine. Fertilizer applied with other herbicides may reduce weed control or cause crop injury. Some fertilizers enhance non-target plant growth to stimulate competition from weed species re-establishing. Fertilizers should be used with herbicides only as indicated on the label or where experience has proven acceptability (USDA Custer NF 2006).

Organosilicones and silicone surfactants are two types of nonionic surfactants. Organosilicone surfactants drastically reduce surface tension of water to the point where the herbicide droplets thin and coalesce to form a thin layer on the leaf surface (known as “superspreading”). In addition, this class of surfactant provides improved effectiveness through maximum rainfastness (Tu et al. 2001).

Table 1. Recommended Adjuvant Type by Herbicide[a]

Herbicide	Recommended adjuvant types
2,4-D	Non-ionic surfactants (NIS), fertilizer, crop oil concentrate
Aminopyralid	NIS
Chlorsulfuron	NIS, seed oil, organosilicone
Clopyralid	NIS, crop oil concentrate
Dicamba	Any as allowed by label
Fluroxypyr	No specific adjuvants are recommended
Glyphosate	NIS
Imazamox	NIS, seed oil, organosilicone
Imazapic	NIS, seed oil, organosilicone
Imazapyr	NIS, seed oil
Imazamox	NIS, fertilizer, seed oil, petroleum/crop oil concentrate
Metsulfuron methyl	NIS, seed oil, organosilicone
Picloram	None needed but can add as per surfactant manufacturer's label
Sulfometuron methyl	Any allowed by label
Triclopyr triethylamine salt (TEA)	NIS

[a] Recommended by Prather et al. 2011, and product labels.

Table 2. Adjuvant Type, Class, Product, and Product Manufacturer[a]

Adjuvant Type	Category	Product Name	Product Manufactor	Principal Functioning Agents	Use Range	Signal Word	Comments
Activator	Non-ionic surfactant (NIS)	Activator 90	Loveland	Alkylphenol ethoxylate, alcohol ethoxylate and tall oil fatty acid	0.125-0.5%	Caution	Low foam, biodegradable, non-flammable
		R-11	Wilbur-Ellis	Alkylphenol ethoxylate, butyl alcohol, dimethylpolysiloxane	0.063-1%	Warning	Spreader, activator
		Spreader 90	Loveland	Alkylpolyethoxy ethers and ethoxylated derivatives	8-64 oz/100 gal	Warning	Spreader
		Super Spread 90	Wilbur-Ellis	Alkyl aryl polyoxyethylene glycols and free fatty acids	0.25-0.5%	Caution	Spreader
Activator	Basic Blend *and* Methylated or Ethylated Vegetable Oil *and* Nonionic Surfactant *and* Nitrogen Source	Renegade	Wilbur-Ellis	Modified vegetable oil, ammonium solution, nonionic surfactant	1-2.5%	Warning	Unique blend, high load of Nitrogen
Activator	Methylated or Ethylated Vegetable Oil	MSO with Leci-Tech	Loveland	Methylated seed oils plus emulsifying surfactants	1-2 pt/A	Caution	MSO and non-ionic
Activator		Syl-tac	Wilbur-Ellis	Organosilicone/ modified vegetable seed oil	0.125-0.375%	Caution	

Adjuvant Type	Category	Product Name	Product Manufactor	Principal Functioning Agents	Use Range	Signal Word	Comments
	Methylated or Ethylated Vegetable Oil *and* Organo-Silicone Surfactant	Phase	Loveland	Methylated seed oil plus organosilicone surfactant	0.125-0.5%	Caution	
Activator *and* Utility Modifier	Nonionic Surfactant *and* Buffering Agent or Acidifier	Super Spread 7000, LI 700	Wilbur-Ellis	Alkyl aryl polyoxyethylene, ethoxylated alcohols, aliphatic polycarboxylate	0.25-4 pt/100 gal	Caution	
Utility Modifier	Colorant	Hi-Light	Becker-Underwood	Proprietary blue colorant	6-32 oz/100 gal	Caution	
		Bullseye	Milliken Chemical	Proprietary blue colorant	0.5 oz/gal	None	
Utility Modifier	Water Conditioning Agent *and* Buffering Agent or Acidifier	Bronc Max	Wilbur-Ellis	AMS/ammonium alkyl aryl sulfonates, polycarboxylic acid	0.125-1%	Caution	Ammonium sulfate (AMS) replacement
Utility Modifier	Water Conditioning Agent	Choice Weather Master	Loveland	Blend of salts of polyacrylic, hydroxy carboxylic, propionic acids, phosphate ester, ammonium sulfate	0.25-0.5%	Caution	AMS, water conditioner

[a]Products currently used on both Forests. For information on the process for adding adjuvants to the list, see section on adaptive management.

Toxicity of Adjuvants

Of the adjuvants discussed in this paper, only two carry the Danger signal word 5 (Entry™ II and LI-700®), which is due to the potential effects to the eyes (severely irritating or corrosive). The bulk of the remainder carry the Caution signal word, while several carry the Warning signal word (again because of potential irritant effects to the skin or eyes). None of these adjuvants carry the poison symbol. All of the adjuvants discussed here are no more than slightly toxic when ingested, inhaled, or absorbed through the skin (Acute Toxicity Categories III or IV). (Bakke, 2007) "Normal" environmental exposure levels of surfactants and emulsifiers to humans… would appear to be negligible based on the extremely high dosages that are typically necessary to cause toxic responses in mammals (Tu et al. 2001).

Testing of LD_{50} (lethal dose, 50% kill) on a range of wildlife shows that while some adjuvants are toxic to wildlife at small concentrations, others are considered "practically nontoxic."

Below is the definition of LC_{50} (lethal concentration, 50% kill) and here are the classification levels. (MDAR 2004)

<1 mg/l: HT (Highly Toxic)
1-10 mg/l : MT (Moderately Toxic)
10-100 mg/l: ST (Slightly Toxic)
100, 1,000 mg/l: PN (Practically Nontoxic)
>1,000 mg/l: IH (Insignificant Hazard)

Table 3. Standard Acute Aquatic Species Toxicity Testing Results (Bakke 2007)

Name	Rainbow Trout 96-hour LC_{50}	Bluegill 96-hour LC_{50}	Daphnia 48-hour EC_{50}	Toxicity Level (done by MM)
Ethoxylated fatty amines				
Alkylphenol ethoxylate-based wetter/spreaders				
R-11®	3.8 – 6 mg/L NOEC 1 mg/L	4.2 mg/L NOEC 1 mg/L	5.7 - 19 mg/L NOEC (population size) 0.25 mg/L	Moderately toxic to fish
Activator 90	NA 1.4 (MDACR 2004)	Guppy (*Poecilia reticulata*?) 12.7 mg/L, NOEC 5.8 mg/L	5.2 mg/L (24 hour) NOEC 1 mg/L	MT
Silicone-based wetter/spreaders				
Sylgard® 309	NA	Fathead minnow >4.6 mg/L	22.9 to >41 mg/L (zero population growth con'c = 18 mg/L)	
Dyne-Amic®	NA	26.9 mg/L	NA	ST
Sticker/Spreaders				
Oils				
MSO®	NA	NA	NA	
Hasten®	74 mg/L	NA	>50 mg/L	Slightly toxic to trout
Blends of vegetable oils and silicone-based surfactants				
Syl-tac™	>5 mg/L	NA	>5 mg/L	MT-ST
Phase™	NA	NA	NA	

Table 4. Standard Mammalian Acute Toxicity Testing Results

Name	Oral LD50	Dermal LD50	Inhalation LC50
Ethoxylated fatty amines			
Entry™ II, POEA	1.2 to 14 g/kg (III)	NA	NA
Alkylphenol ethoxylate-based wetter/spreaders			
R-11®	>3.7 g/kg (NPEO) (III)	>2 g/kg (NPEO) (III)	>25 mg/L (est.) (IV)
Activator 90	3.87 to 5.0 g/kg (III)	>2 g/kg (III)	>1.33 mg/L in males (lowest) (III)
X-77®	3.87 to 5.0 g/kg (III)	>2 g/kg (III)	>1.33 mg/L in males (lowest) (III)
Pro-Spreader Activator	>3.3 g/kg (III)	>2 g/kg (III)	NA
Latron AG- 98® (N)	>5 g/kg (NPE) (IV) 0.79 g/kg (butanol) (III)	>3 g/kg (NPE) (III) 3.4 g/kg (butamol) (III)	NA
Latron AG- 98®	2 g/kg (III)	3 g/kg (III)	NA
Alcohol ethoxylate-based wetter-spreader			
Activator N.F.	NA	NA	NA
Silicone-based wetter/spreaders			
Sylgard® 309	>2 g/kg (III)	>2 g/kg (III)	NA
Freeway®	>2 g/kg (III)	>2 g/kg (III)	NA
Dyne-Amic®	>5.05 g/kg (IV)	>2.02 g/kg (III)	NA
Silwet L-77®	>2.0 g/kg (III)	>2 g/kg (III)	NA
Kinetic	3.3 g/kg (III)	>2 g/kg (III)	NA
Sticker/Spreaders			
Bond®	>5 g/kg (IV)	>2 g/kg (III)	4.73 mg/L (III)
Tactic™	>5 g/kg (IV)	>2 g/kg (III)	>0.19 mg/L (4 hr)
R-56®	NA	NA	NA
Cohere®	NA	NA	NA
Oils			
MSO®	>5 g/kg (IV)	> 4 mg/kg (III)	NA
Hasten®	>5 g/kg (IV)	>5 g/kg (III)	5.79 ml/L (III)
Improved JLB Oil Plus	>5 g/kg (IV)	>3.16 g/kg (III)	NA
Cide-Kick®	>5 g/kg (IV)	NA	>5.16 mg/L (III)
Cide-Kick® II™	>5 g/kg (IV)	>2 g/kg (III)	>90.04 mg/L (IV)
Cygnet Plus	NA	NA	NA
Blends of vegetable oils and silicone-based surfactants			
Syl-tac™	>5 g/kg (IV)	>5 g/kg (III)	>2.07 ml/L (III)
Phase™	>5 g/kg (IV)	>2 g/kg (III)	>0.19 mg/L
Crop Oils and Crop Oil Concentrates			
Kerosene	28 g/kg (IV)	>2 g/kg (III)	NA
Agri-dex®	>5.01 g/kg (IV)	>2.02 g/kg (III)	NA
Mor-Act®	>5 g/kg (IV)	NA	NA
Herbimax®	>5 g/kg (IV)	>2 g/kg (III)	NA
Fertilizer/Surfactant Mixtures			
First Choice® Exciter	NA	NA	NA
Magnify	NA	NA	NA
Class Act® Next Generation	NA	NA	NA
Intensify	NA	NA	NA

Name	Oral LD50	Dermal LD50	Inhalation LC50
Acidifiers			
LI-700®	>5 g/kg (IV)	>5 g/kg (III)	>6.04 mg/L (III)
Tri-Fol	NA	NA	NA
Drift Reduction Agents			
In-Place®	NA	NA	NA
Sinker	>9.8 g/kg	>9.8 g/kg	NA
Defoamers			
Foaminator™	NA	NA	NA
No Foam	NA	NA	NA
No Foam Dry	NA	NA	NA
No Foam® B	>5 g/kg (IV)	NA	NA

Note: NA indicates data was not available. Roman numerals in parentheses indicate the corresponding toxicity category

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